Title
Sulfur-Modulated Tin Sites Enable Highly Selective Electrochemical Reduction of CO2 to Formate

Journal
Joule, 1(4)

ISSN
2542-4351

Authors
Zheng, X
De Luna, P
García de Arquer, FP
et al.

Publication Date
2017-12-20

DOI
10.1016/j.joule.2017.09.014

Peer reviewed

Joule

CellPress

Preview

Breaking Compromises in CO_2 Reduction

Brandon R. Sutherland[1,*]

Electrochemical reduction of CO_2 to formate is a promising approach to utilize intermittent renewable energy for high-value chemical storage and to mitigate carbon pollution. Demanding applied targets for this process require that the reaction is sustained at a high current density with near-unity product efficiency. In this issue of *Joule*, Zheng and De Luna et al. show that incorporating sulfur into tin catalysts greatly increases the reaction rate while maintaining high selectivity and robust stability.

Despite pressure from climate policy initiatives and growing economic incentives for the adoption of renewable power, the world still largely relies on the use of oil, natural gas, and coal to meet its energy demands. These carbon-emitting fossil fuels still account for >85% of global energy consumption today,[1] and even conservative estimates have the total amount of available CO_2 at 5,000 gigatons—enough to last until 2300 at current projected consumption rates.[2] Even aggressive targets such as the Paris Climate Agreement[3] allow for ~700 gigatons of CO_2 emissions from 2017 through 2100.[4] What this means is that for the foreseeable future, there will continue to be significant CO_2 byproduct generation.

To abate the total amount of CO_2 released into the atmosphere over the next century, there is a need for a new force to initiate a step-change in the fossil fuel economy. There are many parallel and compatible approaches toward realizing this; for example, (1) economic and politically driven incentives to displace fossil fuels with renewables; (2) technological breakthroughs leading to large reductions in the $/kWh of clean energy, such as solar electricity; and (3) new technology capable of cost-efficiently converting CO_2 into valuable chemicals such as fuels or precursors for manufacturing.

In recent years—likely as a response to the growing scientific body of knowledge of climate change and its impact on society—the chemical conversion of CO_2 has seen a resurgence of interest from the scientific community. The electrocatalysis of CO_2 through a reduction reaction (CO_2RR) is an attractive approach as it operates at ambient temperature and pressure and is compatible with intermittent renewable energy resources such as solar and wind.

Still in its infancy in terms of commercial relevance, CO_2RR stands to benefit greatly from both increased foundational understanding and continued progress toward improving the efficiency, stability, and scalability of the process. CO_2 is a naturally stable and chemically inert molecule that is challenging to reduce into molecular and atomic constituents. The kinetics of the reaction are slow; therefore, effective catalysts are needed to improve the reaction efficiency. The specific composition and design of a catalyst governs the conversion rate, efficiency, driving voltage, and selectivity toward a given product.

The choice of product remains an important point of consideration. Higher-value products, such as longer-chain hydrocarbons, are challenging to produce. Lower-value products, such as those based on a single carbon, are more realizable based on current technology, but only a few such products have any commercial interest. Formate ($HCOO^-$) is one such product as it is a valuable chemical used as a fuel, for hydrogen storage, and as a feedstock in chemical and drug manufacturing.[5] Some common catalysts that efficiently produce formate include derivatives of Co,[6] Pd,[7] and Sn.[8] However, to date, catalysts that selectively produce formate in lab-scale H-cells have only done so at low current densities. Therefore, there is a need for the development of new catalysts that can selectively convert CO_2 to formate at high reaction rates.

There are several key factors that determine the activity of catalysts, such as the specific geometry, the exposed crystalline facets, and the local coordination environment.[9] Active sites that are undercoordinated often exhibit reduced energetic barriers in the electroreduction of CO_2. Therefore, one promising approach to improving catalysts is to distort the lattice by introducing dopant atoms that reduce the coordination of the active sites. In this issue of *Joule*, Zheng and De Luna et al. have taken this approach and show that Sn-based catalysts for the reduction of CO_2 to formate can be greatly improved through the incorporation of a small amount of sulfur.[10] When coated onto Au nanoneedles, this sulfur-modulated Sn (Sn(S)) catalyst demonstrates excellent catalytic properties for the reduction of CO_2 to formate.

The authors first sought to understand the role of the local environment of Sn

[1]*Joule*, Cell Press, 50 Hampshire Street, 5th Floor, Cambridge, MA 02139, USA

*Correspondence: bsutherland@cell.com

https://doi.org/10.1016/j.joule.2017.12.004

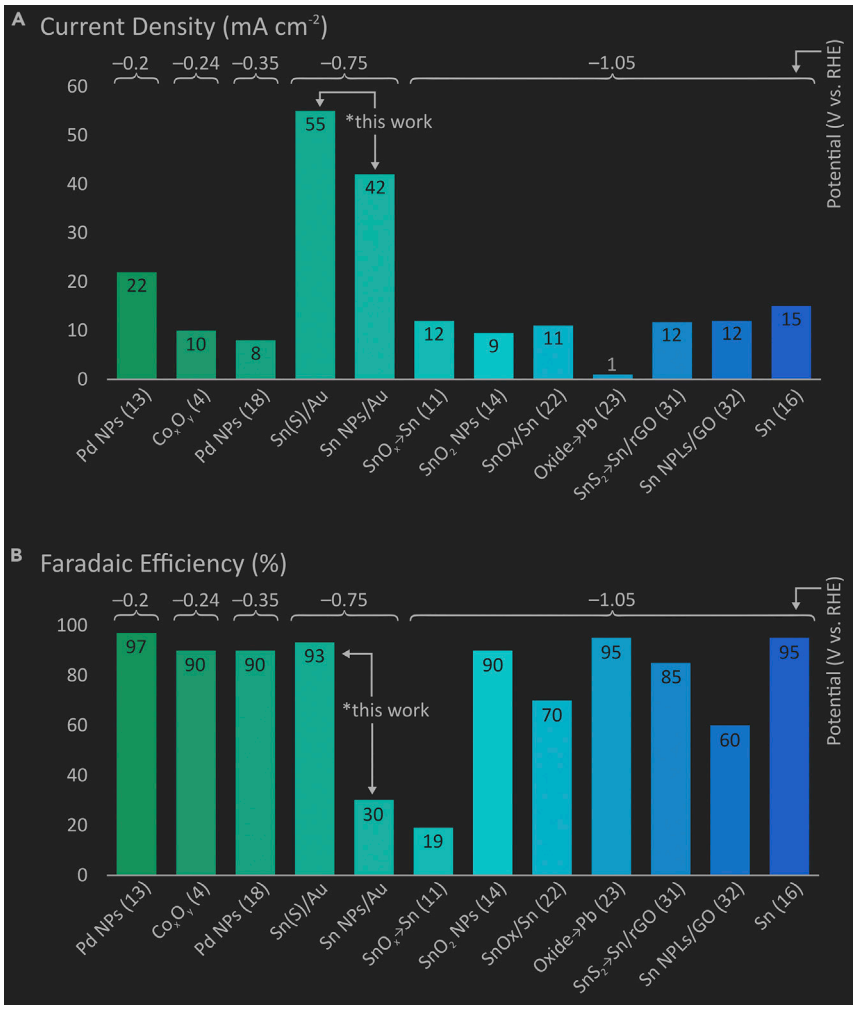

Figure 1. Comparison of Optimized Sulfur-Modulated Tin Electrocatalytic Reduction to Formate with Leading H-Cell Configuration Reports in Literature

(A and B) A simultaneously high (A) current density of 55 mA cm^{-2} and (B) Faradaic efficiency of 93% is achieved with Sn(S) deposited onto Au nanoneedles. References refer to citation number in original manuscript. Acronyms in x axis defined as: NPs, nanoparticles; NPLs, nanoplatelets; GO, graphene oxide; Rgo, reduced graphene oxide; and → implies that the product was derived from the reagent.

on catalytic activity. Using density functional theory (DFT) to model the rate-limiting intermediates in the electroreduction of CO_2 to formate on a Sn slab, they show that formate production is preferred with low incorporation of sulfur (3.8%–25%) into the tin lattice. It is also shown that undesirable CO and H_2 byproducts are unfavorable under these conditions. This analysis motivates the fabrication and systematic study of Sn(S) catalysts for CO_2RR to formate.

The specific choice of substrate—its composition and geometry—is one critical point of control in the engineering of efficient catalytic systems. The use of sharp nanoneedles has been previously shown to concentrate the electric field near the tip of the needle through a field-induced reagent concentration (FIRC) mechanism, resulting in high catalytic activity for CO_2 to CO.[11] The authors therefore investigated the synergy between Sn(S) and Au nanoneedles. They used atomic layer deposition (ALD) to deposit a controlled and uniform layer of SnS_x onto these needles, followed by an electroreduction step to reduce the amount of sulfur to the desired low range for optimal energetics for formate production as determined by their DFT investigation. Due to its high degree of conformality, ALD is an ideal tool to uniformly coat the sharp Au nanoneedles.

The resulting films are polycrystalline with approximate grain sizes of 5 nm. The final material composition is in the range of 3.2%–4.6% elemental sulfur, as measured by X-ray photoelectron spectroscopy. *In situ* X-ray absorption spectroscopy reveals an oxidation state between Sn^0 and Sn^{2+} present at –0.7 V versus reversible hydrogren electrode in Sn(S) that is otherwise not observed in Sn nanoparticles, suggesting that Sn may exist in more oxidized forms despite negative reducing potentials. Based on this analysis, the authors propose that Sn(S) has more undercoordinated sites than Sn nanoparticle controls.

The CO_2RR to formate of Sn(S) catalysts on Au nanoneedles exhibits excellent Faradaic efficiency (93%) and current density (55 mA cm^{-2}) at a potential of –0.75 V versus RHE for formate production. This is significantly higher than controls deposited onto Sn foil, or Sn nanoparticles spin-coated onto Au nanoneedles. It is the highest current density reported to date for CO_2RR to formate in H-cell configurations (Figure 1A), and it achieves this without sacrificing high Faradaic efficiency (Figure 1B). Stability is a critical requirement for any CO_2RR catalyst, and the authors have demonstrated that no degradation in current density is observed over 40 hr of continuous operation.

This work by Zheng and De Luna et al. has shown the importance of the local coordination environment in highly efficient, selective, and stable Sn catalysts. These results motivate several paths

forward for realizing effective CO_2RR to formate catalysis: (1) analogous studies to reduce the coordination of other non-noble metal catalysts with simple binary stoichiometry tuning, (2) continued use of FIRC as a method to realize high current densities without sacrificing other key figures of merit, and (3) the development of application-relevant flow cell systems to further scale the current density. On this basis, the continued exploration of heterogeneous catalyst materials on nanostructured substrates for CO_2RR holds promise in the future of clean energy.

1. BP Statistical Review of World Energy 2017. (2017). https://www.bp.com/content/dam/bp/en/corporate/pdf/energy-economics/statistical-review-2017/bp-statistical-review-of-world-energy-2017-full-report.pdf.

2. Tokarska, K.B., Gillett, N.P., Weaver, A.J., Arora, V.K., and Eby, M. (2016). The climate response to five trillion tonnes of carbon. Nat. Clim. Chang. *6*, 851–855.

3. Paris Agreement (2016). Available at: http://unfccc.int/paris_agreement/items/9485.php.

4. Rogelj, J., Luderer, G., Pietzcker, R.C., Kriegler, E., Schaeffer, M., Krey, V., and Riahi, K. (2015). Energy system transformations for limiting end-of-century warming to below 1.5°C. Nat. Clim. Chang. *5*, 519–527.

5. Verma, S., Kim, B., Jhong, H.-R., Ma, S., and Kenis, P.J.A. (2016). A gross-margin model for defining technoeconomic benchmarks in the electroreduction of CO_2. ChemSusChem *9*, 1972–1979.

6. Gao, S., Lin, Y., Jiao, X., Sun, Y., Luo, Q., Zhang, W., Li, D., Yang, J., and Xie, Y. (2016). Partially oxidized atomic cobalt layers for carbon dioxide electroreduction to liquid fuel. Nature *529*, 68–71.

7. Klinkova, A., De Luna, P., Dinh, C.-T., Voznyy, O., Larin, E.M., Kumacheva, E., and Sargent, E.H. (2016). Rational design of efficient palladium catalysts for electroreduction of carbon dioxide to formate. ACS Catal. *6*, 8115–8120.

8. Zhang, S., Kang, P., and Meyer, T.J. (2014). Nanostructured tin catalysts for selective electrochemical reduction of carbon dioxide to formate. J. Am. Chem. Soc. *136*, 1734–1737.

9. Mistry, H., Varela, A.S., Kühl, S., Strasser, P., and Cuenya, B.R. (2016). Nanostructured electrocatalysts with tunable activity and selectivity. Nat. Rev. Mater. *1*, 16009.

10. Zheng, X., De Luna, P., García de Arquer, F.P., Zhang, B., Becknell, N., Ross, M.B., Li, Y., Norouzi Banis, M., Li, Y., Liu, M., et al. (2017). Sulfur-modulated Tin sites enable highly selective electrochemical reduction of CO_2 to formate. Joule *1*, this issue, 794–805.

11. Liu, M., Pang, Y., Zhang, B., De Luna, P., Voznyy, O., Xu, J., Zheng, X., Dinh, C.T., Fan, F., Cao, C., et al. (2016). Enhanced electrocatalytic CO2 reduction via field-induced reagent concentration. Nature *537*, 382–386.

Preview

Better Semiconductor-Catalyst Interfaces Using Light

Qiushi Yin[1] and Craig L. Hill[1,*]

Searching for stable and high-performing photoanode materials is a key challenge for photoelectrochemical water splitting. In this issue of *Joule*, He and coworkers report a novel interface between Ta_3N_5 and $Co(OH)_2$ that forms under photoelectrochemical conditions. A synergistic interaction between semiconductor and water oxidation catalyst gives rise to improved performances in both photovoltage and stability.

The photoelectrochemical splitting of water or reduction of CO_2 by water remains the principal, potentially practical approach to generate H_2 and reduced carbon molecules ("solar fuel"). Effective PEC devices require electrode materials that absorb light intensely and broadly to generate long-lived, charged-separated excited states at the semiconductor-electrolyte interface.[1] Compounding this fabrication challenge is the requirement that the oxidizing (photoanodic) surface must catalytically oxidize water, and the reducing (cathodic or photocathodic) surface must catalytically reduce water or CO_2. Understanding how to construct these semiconductor-catalyst interfaces and control their charge transfer properties is critical for the scalable preparation of maximally efficient and stable photocatalytic water oxidizing electrodes and thus PEC devices.[2]

Construction of a stable high-performance photoanode for a functional photoelectrochemical cell (PEC) remains the key challenge for researchers in the renewable energy field. Issues of effective charge separation involving the oxygen evolution reaction as well as the oxidative stability of the semiconductor material are crucial for achieving a high photovoltage. Many of the relevant chemical interactions dictating most of these properties originate at the semiconductor/liquid interface (SCLI). Major effort has been dedicated to clarifying the specific chemistry that occurs at the SCLI.

Ta_3N_5 is a potentially attractive direct bandgap semiconductor material for

[1]Department of Chemistry, Emory University, Atlanta, GA 30322, USA

*Correspondence: chill@emory.edu

https://doi.org/10.1016/j.joule.2017.12.006